Energy landscape, two-level systems and entropy barriers in Lennard-Jones clusters

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We develop an efficient numerical algorithm for the identification of a large number of saddle points of the potential energy function of Lennard- Jones clusters. Knowledge of the saddle points allows us to find many thousand adjacent minima of clusters containing up to 80 argon atoms and to locate many pairs of minima with the right characteristics to form two-level systems (TLS). The true TLS are singled out by calculating the ground-state tunneling splitting. The entropic contribution to all barriers is evaluated and discussed.

The use of an effective potential energy to describe the dynamical properties of disordered systems has become a very powerful tool of investigation. In particluar, there is broad consensus on the idea that important relaxational processes can be described by transitions between adjacent potential-energy minima in the multidimensional configuration space. The latter, however, is so complex even for systems containing a moderate number of atoms, that singling out relevant pairs of minima has required important numerical efforts and skill by many authors [1–7]. One of the goals of this kind of research is the identification of pairs of minima suitable to produce two-level systems (TLS); these are the pairs of nearly degenerate minima separated by a barrier that, following tunneling, produces a total splitting of the order of $\approx< 1$ K, thus explaining the anomalous low-temperature specific heat and thermal conductivity of glasses [8–10].

Identifying adjacent minima is not simple by molecular dynamics methods; it is clear that the key stationary points are not the minima but rather the (first-order) *saddle points*, descending from which adjacent minima are automatically found. But there are other reasons why the search for saddle points looks desirable, which are in a way or another related to the fact that the minimum-minimum relaxation process takes place along a classical path that passes close to the saddle, i.e. the least-action path.

The first reason is that evaluating the TLS ground state splitting is a quantum mechanical problem, but the solution of the Schroedinger equation in $3N$ dimensions is out of question and one is forced to think of ways of drastically reducing the dimension of the problem, possibly to one. It is therefore necessary to have an indication about how much and under which circumstances this reduction is feasible; as we will discuss later this kind of information requires a detailed knowledge of the path along which tunneling is considered to take place and of the potential energy along it.

The second reason, which is related to the first one, is that relaxation processes of all kinds, either the low-temperature ones that produce TLS or the high-temperature ones that govern the glass transition, in principle are controlled not only by energy barriers, but also by *entropy* barriers, i.e. by the topological difficulty of proceeding from one minimum to another through a narrow route even in the absence of potential energy barriers [11–13]. Note that entropy barriers would also affect the quantum mechanical splitting of the ground state in much the same way as energy barriers do [14].

Heuer [7] has recently studied the potential-energy topology of systems containing 32 atoms placed in a box with periodic boundary conditions and interacting through a Lennard-Jones-like potential introduced in ref. [1]. At a numerical density $\rho = 1$ in units of the nearest neighbor distance, the author finds 367 minima of different energy, which become 75 by decreasing the box size by $\approx$2%. These values are exceedingly small when compared to the $\approx 10^{11}$ different minima expected for a Lennard-Jones cluster of 32 atoms [15]: the boundary conditions have a dramatic effect on the number of minima (and probably of all kinds of stationary points). Heuer [7] notes that performing the simulation at variable box length produces many more minima; in view of this situation, we think it is very important to search for the stationary points in the absence of any boundary condition, i.e. for free clusters. The reason is that even periodic boundary conditions with variable density are likely to introduce spurious correlations among different boxes, that might affect the results. The price to be paid is the presence of surface effects which (like the correlations of the boundary conditions case) become less and less important as the system size is increased.

The systems we studied are Ar clusters with up to N =80 atoms, interacting through the Lennard-Jones potential

$$V(\mathbf{r}) = 4\epsilon \sum_i \sum_{j>i} [(\frac{\sigma}{r_{ij}})^{12} - (\frac{\sigma}{r_{ij}})^6]$$

with $\sigma = 3.405$ $\mathring{A}$ and ϵ/k_B=125.2 K.

Since we think of our clusters as parts of a glass, in which case translations and rotations are forbidden, we

decided to set six coordinates to zero (one atom is fixed in the origin, one on the x axis and one on the xy plane) in order to eliminate translations and rotations. Free translations of the system as a whole are decoupled by other degrees of freedom, but in non-rigid bodies like clusters rotations and vibrations are coupled. Therefore, the above conditions leave the potential energy of the stationary configurations unaffected because it depends only on mutual distances, but the elimination of rotations affects vibrational frequencies by altering the effective mass. We do not expect any systematic bias of the results because the coordinates to be fixed are chosen at random.

The saddle points were found with the procedure described in detail in ref. [15], and which consists of the following steps: (i) descent towards a minimum by the conjugate gradient method, starting from a randomly chosen configuration; (ii) ascent towards the vicinity of a saddle following the eigenvector corresponding to the minimum eigenvalue of the Hessian; this requires diagonalization of the Hessian at each step; (iii) once the potential energy along the path of the previous item starts decreasing, we take the corresponding configuration as the starting point for a Newton- Raphson stationary point search [16]. This means that the non linear system of equations

$$\frac{\partial V(\mathbf{r})}{\partial x_i} = 0 \qquad (1)$$

is solved by successive iterations for i=1...(3N-6). The steps ($i-ii$) are required in order that the Newton procedure converges; the iteration ends up in a first order saddle in about 30% of cases and the saddle is located with extreme accuracy. The next step is a minimum-eigenvalue descent on both sides of the saddle, which provides approximate *adjacent* minima that are subsequently fed into the Newton algorithm for accurate location. With this numerical procedure we found many thousand minimum-saddle-minimum triplets for several values of N in the range 6-80. The number of triplets found and of those with asymmetry Δ¡1 K, are reported in the second and third columns of Table I, respectively. The last 2 columns of the Table entail the evaluation of the ground state splitting, which will be discussed later.

The first check we performed was to look for correlations between the asymmetry and the barrier height; contrary to previously reported results on periodic systems [4,20] we found no correlation. The pairs of minima were further characterized by their euclidean distance, d, and by the participation number, $N_p = d^2/d^2_{max}$, where d_{max} is the displacement of the atom that moves most. The distribution of d is peaked at $\approx 4\sigma$ for $N = 13-42$ and at $\approx 6\sigma$ for $N = 80$, with tails extending up to $\approx 15\sigma$. These tails reflect the free- surface effects that we know affect the clusters, but interestingly enough the TLS pairs have in all cases $d <\approx 2\sigma$. This is convenient for an a priori selection of candidate TLS. The participation number for $N = 42, 80$ is reported in Fig. 1. In column (b) of Table I we report the number of candidate TLS, i.e. those triplets that have both Δ¡1 K and the barrier higher than the lowest vibrational eigenvalue of either minimum; the distribution of their participation number is not very different from that of all pairs for $N \leq 42$, while for $N = 80$ we have too few pairs to draw any definite conclusion.

In order to identify the TLS, we need the total splitting of the ground level, resulting from asymmetry, Δ, and tunneling, δ_T. As mentioned above, the evaluation of the latter is a quantum mechanical issue and can be solved relatively easily only if the many- dimensional dynamics can be reduced to a 1-dimensional one. If this is at least approximately feasible, then the computationally most convenient way of evaluating δ_T is to use the semiclassical WKB approximation [17,18] that provides an explicit expression in terms of the potential energy profile $V(x)$:

$$\delta_T = \frac{\hbar\omega}{\pi} D^{1/2} \qquad (2)$$

with $D = [1 + exp(2S)]^{-1}$ and the action integral $S = \frac{1}{\hbar}\int_a^b \{m[2V(x) - \hbar\omega]\}^{1/2} dx$ is evaluated between the classical turning points a and b; ω is the classical frequency in one well. The total splitting is then obtained as $\delta \approx \sqrt{\Delta^2 + \delta_T^2}$. As mentioned, in principle it is possible to use equation (2) for evaluating the tunneling splitting only if the Schroedinger equation can be separated into independent ones for each degree of freedom [19]; we shall assume that (2) can be employed under the less restrictive condition that the *relevant* classical degree of freedom, i.e. the coordinate along the least action path, is decoupled by the remaining ones. Demichelis et al [14,20] first found that this actually occurs for argon with periodic boundary conditions, and the same has been verified for candidate TLS in clusters [21]: the higher vibrational eigenvalues, obtained by diagonalizing the dynamical matrix at configurations along the least-action path, do not change appreciably along the path itself, while the ground one obviously does. Under these circumstances the use of Eq. (2) is reasonably justified [19]. The least-action path was determined by minimizing the action integral S following the procedure of ref. [14], and by taking as initial path the one starting from the saddle and reaching the minima by a minimum eigenvalue search. The action integral was evaluated also along the straight line connecting the minima; for the TLS the straight-line integral turns out to be only a factor 2-5 larger than the least-action one.

In the last column of Table I (TLS) we report the number of triplets that have a total (asymmetry plus tunneling) splitting in the ground state $\delta < 1$ K, and thus have all the characteristics of TLS [22]. We see that interestingly enough the category of TLS almost coincides with that of column (b). But most remarkably, it seems that

n(TLS)/n(Total) is roughly of the order of 10^{-3} and apparently tends to increase with N; if this trend should be confirmed it would mean that surface effects *do not* favor TLS, so that the failure to observe them in periodic systems of comparable [7] or larger [20] size should probably be ascribed either to correlations or to density. In any case, visual inspection of the TLS relative to $N = 80$ shows that surface effects are still very important because in all 3 cases there is at least one surface atom that moves most. For $N = 42, 80$ we verified that TLS are isolated, in the sense that we did not find any low-barrier route that connects one minimum of the pair to a third almost degenerate minimum. This was to be expected since only $\approx 1/100$-th of the pairs are nearly degenerate (Table I, column (a)).

The entropic contribution to classical relaxation was considered along the following lines. The classical one-dimensional transition rate between minima separated by a barrier E_b is

$$k = \frac{\omega}{2\pi} exp(-\frac{E_b}{K_B T}) \tag{3}$$

where ω is the vibration frequency in the potential well; in many dimensions and under some assumptions concerning thermodynamic equilibrium and the absence of back crossing, it is found that the entropic-barrier effect of degrees of freedom other than the single considered path can be accounted for by the following substitution in the pre-exponential factor of (3) [23–25]:

$$\omega \rightarrow \Pi_i \omega_i^M / \Pi'_j \omega_j^S = \frac{\omega}{R} \tag{4}$$

Here ω_i^M and ω_j^S are the vibrational eigenfrequencies at the minimum and at the saddle respectively, and the prime indicates that the imaginary frequency at the saddle point has to be omitted from the product.

The entropic ratio R has been calculated for all minimum-saddle-minimum triplets for $N = 42$ and 80, and is reported for $N = 80$ in fig. 2 as a function of the barrier. For N =42 the distribution is qualitatively similar but much more scattered. As can be seen, the majority of the triplets have R in the range 1-10^{-2}, with a high-barrier tail extending down to $R \approx 10^{-6}$. Only relatively few triplets (0.45%) have $R > 1$ (but in any case not exceeding the value 10); for N =42 this fraction becomes 0.75%. The present results seem to indicate that entropic barriers are not especially active in slowing down the relaxation dynamics, and that the effect may become less important with increasing N. This result is contrary to what found recently for a different model of fragile glass with periodic boundary conditions [26]: the role of boundary conditions on the results of simulations on relatively small systems definitely deserves further investigation.

For the TLS, in agreement with the reported independence of the eigenvalues other than the ground one on the position along the least-action path [20], we find $R \approx 1$. Considering that for N =80 R is the ratio of two products of 234 numbers each, the result $R \approx 1$ is remarkable and shows that TLS belong to a rather peculiar class of triplets. In this case, entropic barriers do not play a relevant role in determining the quantum splitting of the ground level, though in general they quench the splitting like ordinary potential barriers.

In summary, TLS have been shown to exist in Lennard-Jones clusters and have been characterized; the order of magnitude of the ground level quantum splitting has been evaluated by means of the semiclassical 1-dimensional WKB formula; topological hindrances do not play a significant role in determining this splitting. Moreover, the relaxation dynamics of the vast majority of minimum-saddle-minimum triplets appears to be little affected by entropic barriers. As far as we are aware, this kind of information on tunneling and relaxation processes has not been provided before, and it was made possible by the use of a numerical procedure that produces a large amount of adjacent minima. The quantitative application of these results to glasses requires great caution, because surface effects are certainly present in our clusters. However, the influence of boundary conditions and density on the properties of the landscape [7] is also very great and the present zero-pressure and correlation-free results may certainly help in getting a closer insight into the problem.

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TABLE I. Number of pairs of adjacent minima found for $N = 6 - 80$. Δ is the asymmetry and δ the total splitting of the ground state (see text). (a): $\Delta < 1$ K; (b): Same as (a) but with barrier higher than minimum vibrational eigenvalue; (TLS): same as (b) but with total splitting $\delta < 1$ K and tunneling splitting $\delta_T > 10^{-15}$ K (see ref. [20]).

N	Total	(a)	(b)	TLS
6	6	0	0	0
8	61	0	0	0
9	181	4	0	0
10	414	2	0	0
13	3416	41	3	3
15	4652	43	6	4
18	11412	150	19	15
29	9176	63	18	13
42	2878	31	11	7
80	1290	9	3	3

FIGURE CAPTIONS

Fig. 1. Participation number for clusters with $N = 42$ (squares) and 80 (circles).

Fig. 2. Entropic ratio R, as defined in Eq. (4), for $N = 80$ as a function of the saddle-minimum energy barrier; full circles: upper minimum; open squares: lower minimum.

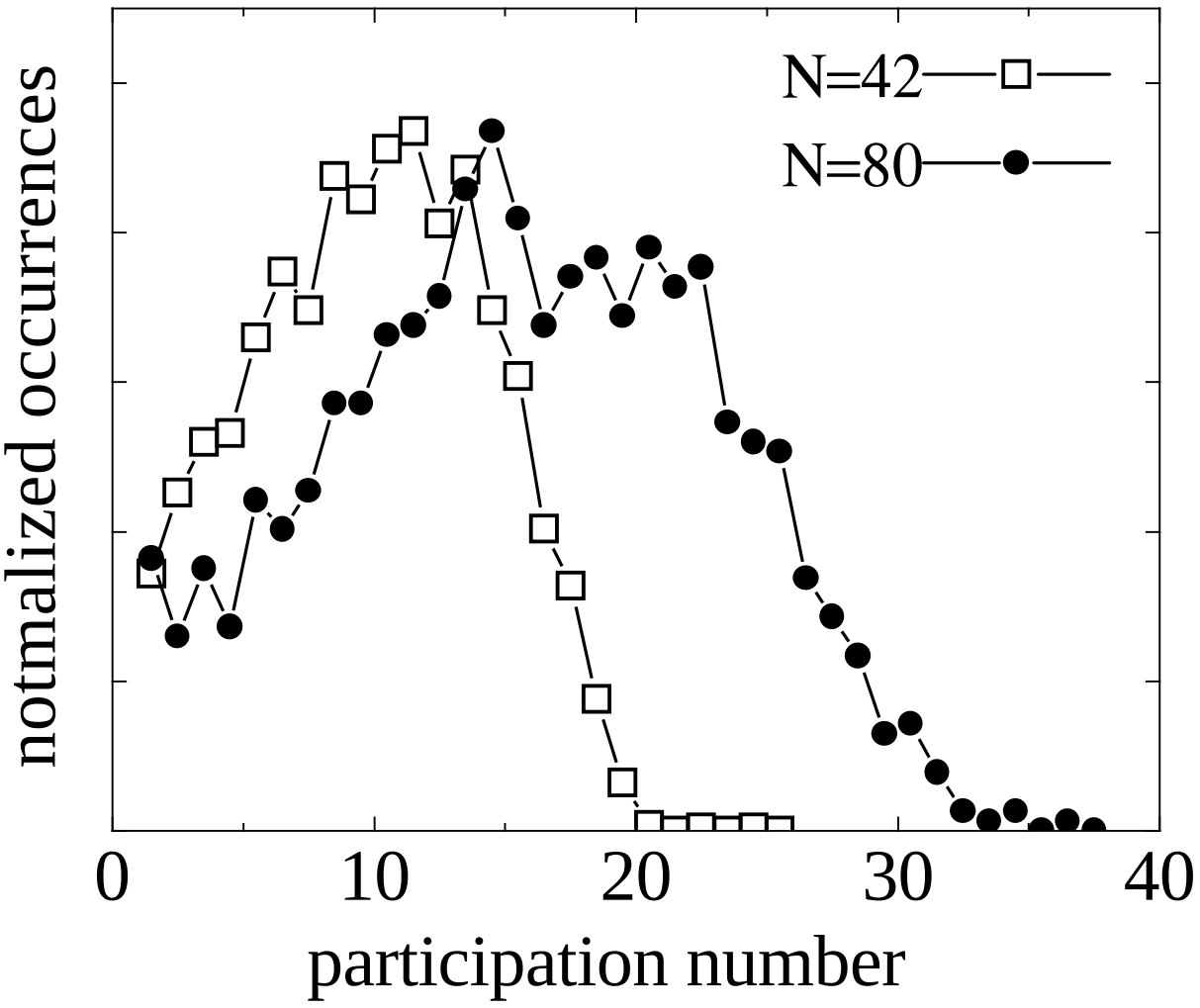

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Figure 1

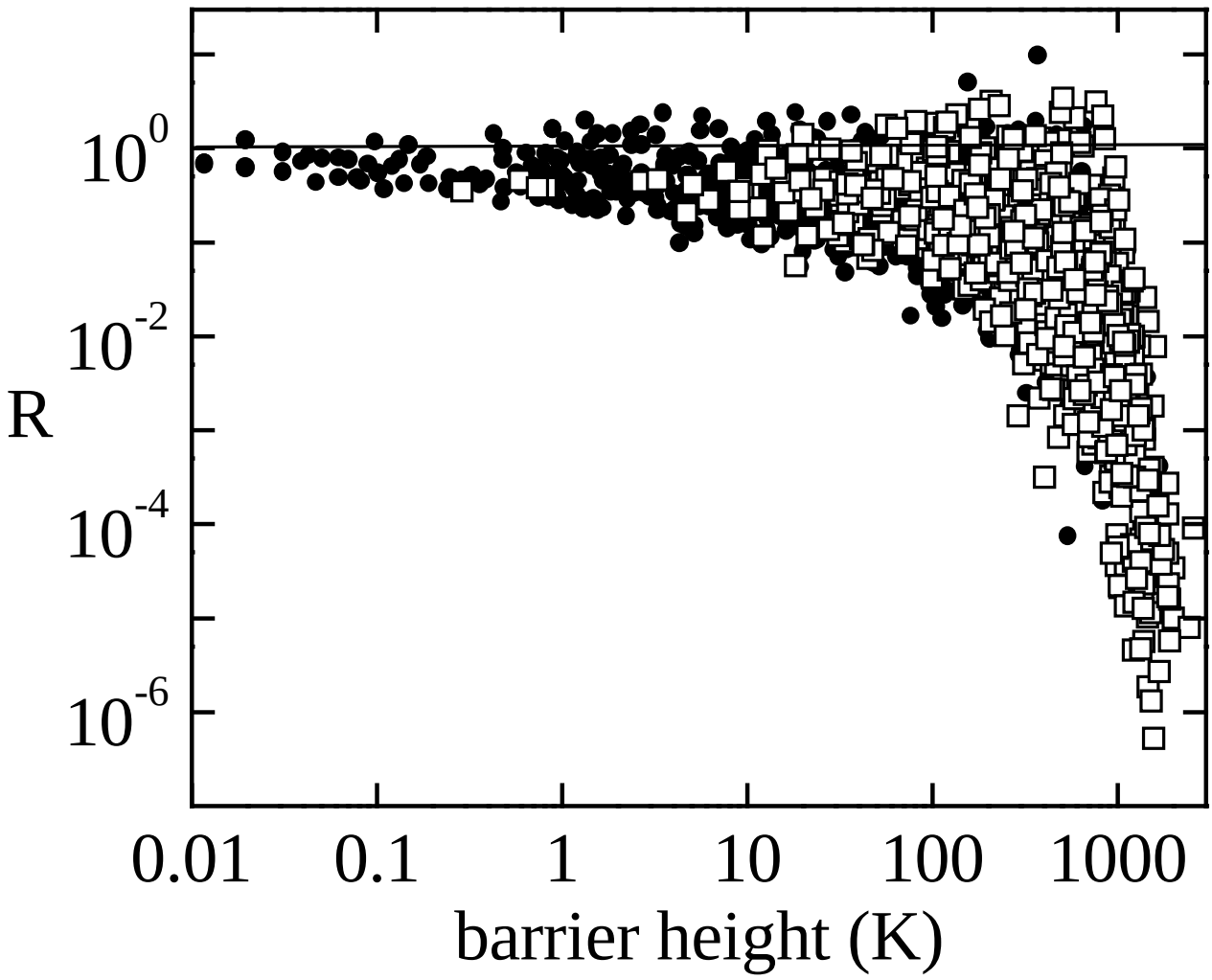

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Figure 2